Gas Chromatography of Metal Chelates Using the LVGC Method : Nickel(II) Trifluoroacetylacetonate (Commemoration Issue Dedicated to Professor Tsunenobu Shigematsu on the Occasion of his Retirement)

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Bull. Inst. Chem. Res., Kyoto Univ., Vol. 58, No. 2, 1980

Gas Chromatography of Metal Chelates Using the LVGC* Method

——Nickel (II) Trifluoroacetylacetonate——

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Received February 8, 1980

The gaschromatographic behavior of Ni(TFA)$_2$ chelate (H-TFA; trifluoroacetylacetone) was fundamentally investigated by using the LVGC method. It was found that Ni(TFA)$_2$ chelate was completely separated from various metal-TFA chelates by using a mixed-liquid phase column of 1.95% OV-17+0.05% PEG20M, and that Ni(TFA)$_2$ chelate was completely eluted by using the LVGC method. Based on the results of this fundamental investigation, this method was applied to the analysis of nickel in steel.

KEY WORDS: Nickel(II) trifluoroacetylacetonate/ Manganese(II) trifluoroacetylacetonate/ LVGC method/ Mixed-liquid phase column/

INTRODUCTION

Since beryllium, aluminium and chromium acetylacetonates were successfully gaschromatographed, the gaschromatographic elution and thermal properties of many metal β-diketonates have been extensively investigated. However, the analytical utility of the gas chromatography of metal chelates has been limited except for a few cases, because most of metal chelates are not eluted quantitatively due to thermal decomposition or the adsorption to column packings.

In general, it is well known that the gaschromatographic elution of nickel β-diketonates is difficult under conventional conditions even if fluorinated β-diketone chelates are used as a sample. In order to overcome the facts, Barratt *et al.*[1] studied the gaschromatographic behaviors of nickel monothiotrifluoroacetylacetonate which is a thermally stable monomeric chelate and soluble in non-polar organic solvents. Belcher *et al.*[2-4] and Uden *et al.*[5,6] investigated nickel chelates of β-ketoimine derivatives which are more volatile chelates than fluorinated β-diketonates, and show greater volatility differences between different metal chelates of the same ligand, and are easily preparative owing to rapid reaction with transition metal in solution. The gas chromatography of ternary complexes of a metal-HFA-DBSO system was also investigated by T. P. O'Brien *et al.* [7] to improve solvent extraction properties of metal chelates from aqueous solutions.

On the other hand, the authors previously studied the LVGC method containing

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ligand vapor in helium gas and succeeded in the elution and the separation of many metal fluorinated β-diketone chelates.[8-12]

In the present paper, the fundamental investigation of $Ni(TFA)_2$ chelate using LVGC method is described, and the gaschromatographic method is applied to the determination of nickel in steel.

EXPERIMENTAL

Apparatus and Chromatographic Columns

The gas chromatograph used in this study was Model G1800-T (Yanagimoto Mfg. Co., Ltd.) with a thermal conductivity detector equipped with a ligand-vapor generator, and the gas chromatograms were recorded by a Model VP-653B pen-recorder (Matsushita Communication Ind. Co., Ltd.) and an integrator Model C-RlA (Shimadzu Seisakusho Ltd.). The thermogravimetric analysis of $Ni(TFA)_2$ was carried out by using the injection port of a Model GC-6A gas chromatograph (Shimadzu Seisakusho Ltd.).

The Pyrex glass columns (1. 0m×2. 5mm i. d.) packed with Chromosorb W AW DMCS (60/80 mesh) coated with Apiezon L, silicone DC-550, OV-17, OV-25, and the mixed-liquid of OV-17 and PEG20M were used respectively in the fundamental investigations.

The flow rates of helium carrier gas or helium carrier gas containing ligand vapor were measured by a soap film flowmeter.

Reagents and Preparation of Nickel Chelate

Trifluoroacetylacetone (1, 1, 1-trifluoro-2, 4-pentanedione, H-TFA) was obtained commercially and purified by distillation at 107°C.

G. R. Nickel(II) nitrate hexahydrate was used without further purification. Ni^{2+} standard solution (Ni^{2+} 1. 018 mg/ml) was prepared as follows. Nickel metal (purity 99. 99%, 203. 6mg) was dissolved in 3 ml of concentrated hydrochloric acid, and diluted with distilled water to 200 ml.

$Ni(TFA)_2$ chelate was prepared as follows; To an aqueous solution of nickel nitrate in a 50 ml centrifuge tube, excess sodium hydroxide solution was added. The precipitate of nickel hydroxide was washed well with distilled water. Excess H-TFA reagent was added to the wet precipitate, and the solution obtained was concentrated gently on a hot plate, and nickel hydroxide was converted to $Ni(TFA)_2$ chelate. The viscous solution was cooled to room temperature, and the crystal was obtained by the addition of a few drops of distilled water. Excess H-TFA was removed by extraction with *n*-hexane or *iso*-octane. The product was recrystallized from ethyl acetate. Anal. Calcd. for $Ni(TFA)_2 \cdot 2H_2O$; C=29. 96%, H=3. 02%, F=28. 43%, Ni=14. 64%. Found; C=30. 14%, H=3. 03%, F=28. 52%, Ni=14. 35%. The yield of $Ni(TFA)_2$ chelate was relatively higher.

Sample solutions were prepared by dissolving the purified chelate into *n*-butyl acetate.

All other reagents were of special reagent grade for chemical analysis.

RESULTS AND DISCUSSION

Thermal Properties of Ni(TFA)$_2$ Chelate

The thermal properties were measured by using the injection port of a gas chromatograph GC-6A and an inserting glass tube. The chelate (10 - 20mg) was placed in the inserting tube which was made of Pyrex glass, and both ends of the sample tube were stoppered with glass wool. The tube was precisely weighed on a chemical balance, and was inserted into the injection port of the gas chromatograph GC-6A which was held at a constant temperature. After carrier gas was passed through the tube for 15 minutes, the tube was taken out of the injection port. After cooling to room temperature the tube was weighed again. The weight loss of the sample was measured with the rise of temperature at the injection port for each 30°C.

The relation between the weight loss of the chelate and heating temperature is shown in Fig. 1. In an atmosphere of helium gas, the sample was sublimed at about 140°C, and the residue of about 20% of the sample was left in the inserting tube at about 270°C. On the other hand, under the condition of the atmosphere of helium containing ligand vapor, it was found that nickel chelate was sublimed completely at about 200°C. From these facts it is confirmed that the use of the LVGC method is essential to gas-chromatographic elution of Ni(TFA)$_2$ chelate.

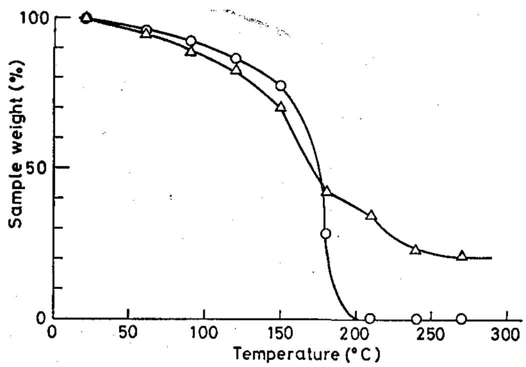

Fig. 1. Thermogravimetric curves for Ni(TFA)$_2$ chelate. Sample taken: (○) 15.4 mg, (△) 11.8 mg, Atmosphere: (○) helium+H-TFA vapor, (△) pure helium, Flow rate 30 ml/min.

Fundamental Investigation of Gas Chromatography of Ni(TFA)$_2$ Chelate

Choice of stationary liquids:

In order to investigate the effect of the polarity of loading liquids on the elution of Ni(TFA)$_2$ chelate, the characterization of 3% slightly-polar silicone liquids of DC-550 (25% phenyl), OV-17 (50% phenyl) and OV-25 (75% phenyl) were examined at a column temperature of 180°C. Each chromatogram is shown in Fig. 2. As is evident from this figure, the leading of peak was considerable in the liquid containing the 25% phenyl group, but was suppressed with increase of the phenyl group from 50% to 75%.

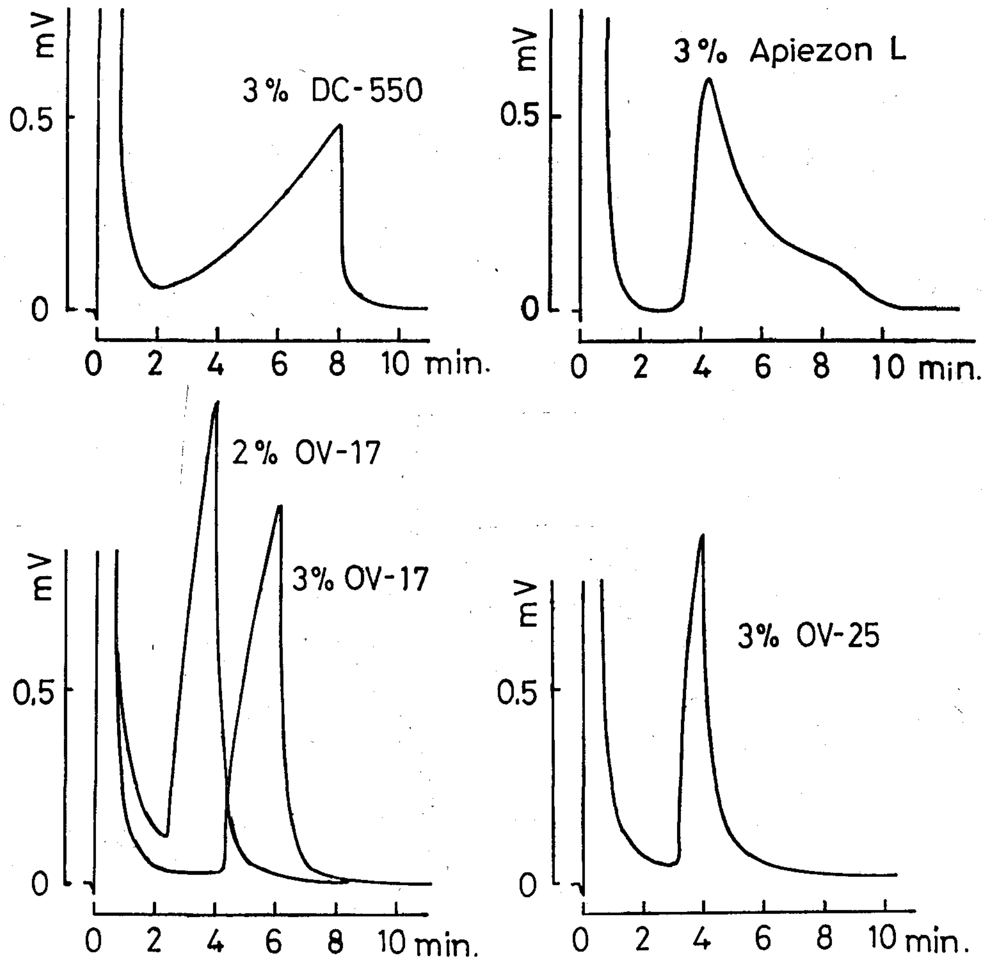

Fig. 2. The effect of the polarity of stationary liquids on the elution of $Ni(TFA)_2$ chelate. Column: 2.5 mm i.d.×1m Pyrex glass, Support: Chromosorb W AW DMCS (60/80 mesh), Inj. and TCD temp. 250°C, Column temp. 180°C, TFA bath temp. 23.0°C, Flow rate 17.3 ml/min, Sample size 15 μl (Ni 30 μg).

On the other hand, when the liquid phase of 3% Apiezon L(non-polar) was used, $Ni(TFA)_2$ chelate was eluted easily at the lower column temperature, but the tailing of the peak was considerable.

When the loading amount of OV-17 was reduced from 3% to 2%, the $Ni(TFA)_2$ peak was overlapped with the solvent peak.

From these facts mentioned above, it was decided that the liquid phase of 3% OV-17 was successful for the gas chromatography of $Ni(TFA)_2$ in the absence of many other heavy metal chelates. The relation between the retention times of metal-TFA chelates and the column temperature was investigated using a 3% OV-17 loading column. The results are shown in Fig. 3. As shown in this figure, $Ni(TFA)_2$ chelate was able to be separated from various metal chelates, but it was found that the separation of peaks of $Mn(TFA)_2$ and $Ni(TFA)_2$ chelate was impossible because of their similar retention time.

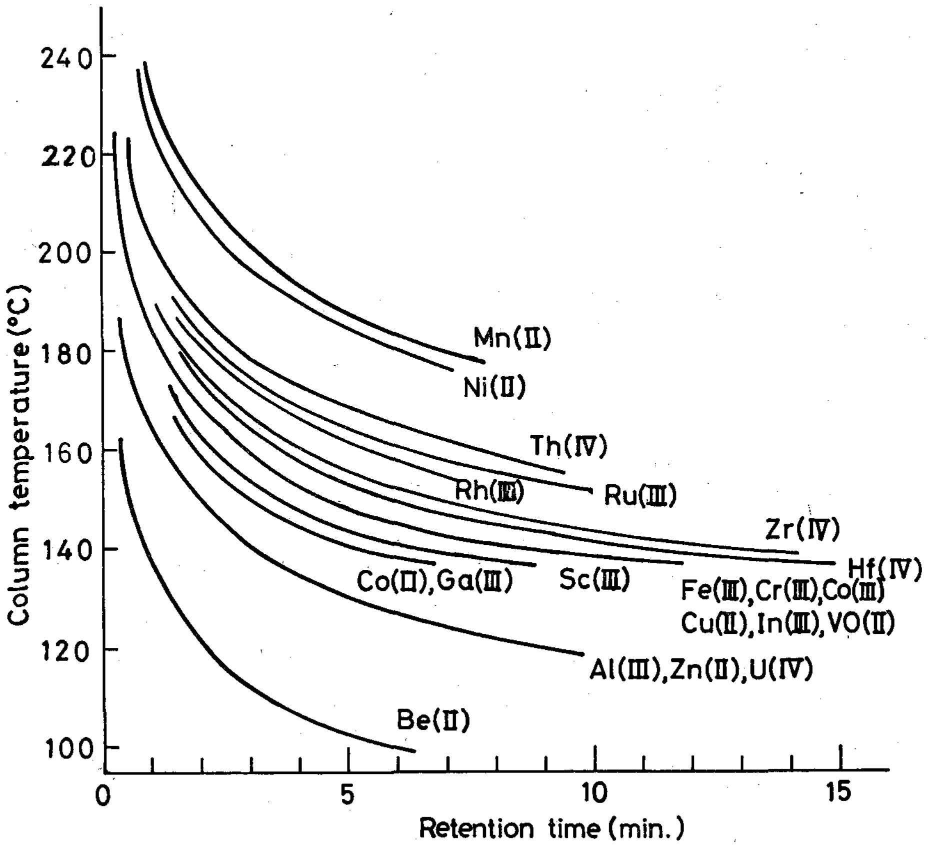

Fig. 3. The relation between the retention times of metal-TFA chelates and the column temperature. Pyrex glass column (1 m×2.5 mm i. d.) packed with 3% OV-17 on Chromosorb W AW DMCS (60/80 mesh) Inj. and TCD temp. 250°C, TFA bath temp. 23.0°C, Flow rate: 17.3 ml/min.

Moreover, the peak area of Ni(TFA)$_2$ chelate was decreased with the increase of the amount of Mn(TFA)$_2$ chelate, as shown in Fig. 4.

In order to eliminate the interference of Mn(TFA)$_2$ chelate on the elution of Ni(TFA)$_2$ chelate, the separation of Ni(TFA)$_2$ and Mn(TFA)$_2$ was investigated by using the mixed-liquid phase of OV-17 and PEG20M. The relation between the ratio of OV-17 to PEG20M and the resolution of these chelates' peaks $(R=2(t_R^{Ni}-t_R^{Mn})/(w_{Ni}+w_{Mn}))$ at various column temperature is shown in Fig. 5. It was found that the peaks of Ni(TFA)$_2$ and Mn(TFA)$_2$ were able to be separated by using the mixed-liquid of 1.95% OV-17+0.05% PEG20M at a column temperature of 220°C or 230°C. The chromatograms of Ni(TFA)$_2$ chelate at 230°C is shown in Fig. 6.

Likewise, the relation between the retention times of various heavy metal chelates and the column temperature was investigated by using mixed-liquid loading. As shown in Fig. 7, Ni(TFA)$_2$ chelate was separated completely from VO(II), Cr(III), Mn(II), Fe(III), Co(II), Cu(II), Zn(II), Th(IV), U(IV)-TFA chelates at a column temperature of 230°C.

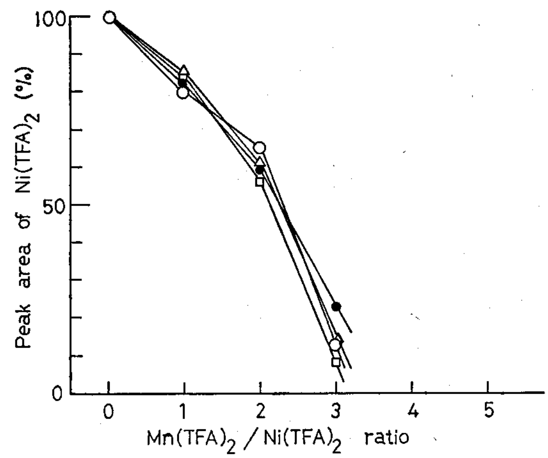

Fig. 4. The effect of $Mn(TFA)_2$ on the elution of $Ni(TFA)_2$. Stationary liquid: 3% OV-17. Gaschromatographic conditions are the same as in Fig. 2. Solvent: (○) *n*-butyl acetate, (△) methyl *iso*-butyl ketone, (□) *iso*-amyl alcohol, (●) *iso*-propyl ether.

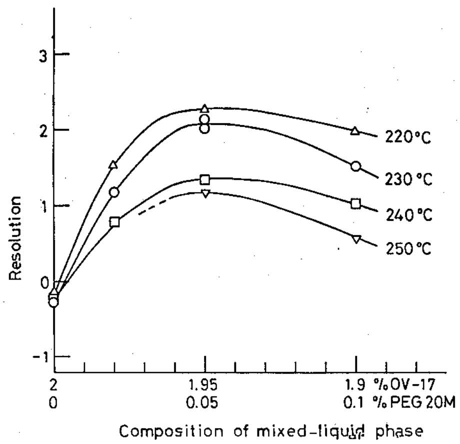

Fig. 5. The effect of the polarity of the liquid phase and the column temperature on the separation of $Ni(TFA)_2$ and Mn $(TFA)_2$.
Pyrex glass column (1.0m×2.5mm i.d.) packed with 2% (OV-17+PEG20M) on Chromosorb W AW DMCS (60/80 mesh). Inj. and TCD temp. 250°C, TFA bath temp. 23.0°C, Flow rate 41 ml/min.

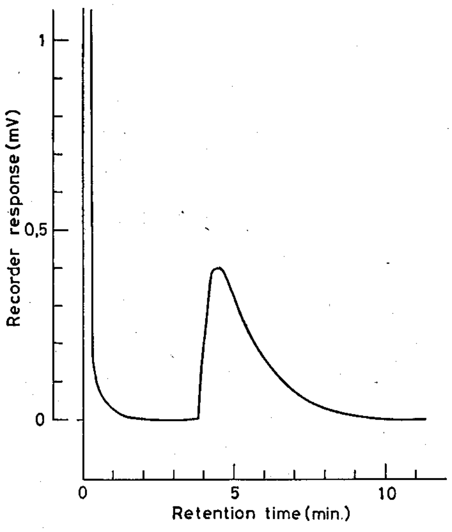

Fig. 6. Typical gaschromatogram of $Ni(TFA)_2$ chelate. Pyrex glass column (1.0m× 2.5mm i.d.) packed with 1.95% OV-17+0.05% PEG20M on Chromosorb W AW DMCS (60/80 mesh). Inj. and TCD temp. 250°C, Column temp. 230°C, TFA bath temp. 23.0°C, Flow rate 41ml/min, Sample size: 10μl (Ni 20 μg), Solvent: *n*-butyl acetate.

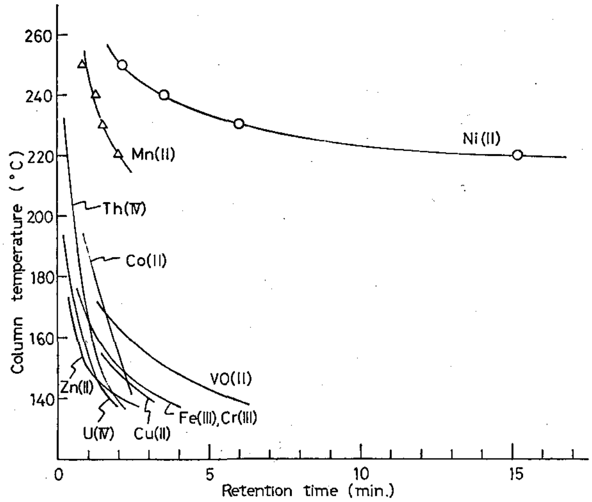

Fig. 7. The relation between the retention times of metal-TFA chelates and the column temperature. Gaschromatographic conditions are the same as in Fig. 6.

Effect of column temperature:

In order to find the optimum temperature of the mixed-liquid phase column of OV-17 and PEG20M, the column temperature was changed from 220°C to 250°C under the flow rate of 41 ml/min. The result is shown in Fig. 8. From the results, it was found that $Ni(TFA)_2$ chelate was eluted quantitatively at higher column temperature than 220°C. Hence, the column temperature was fixed at 230°C for the following experiments.

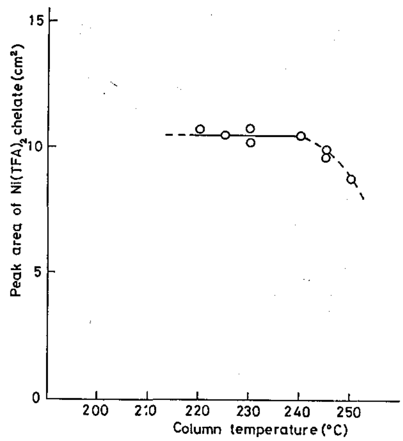

Fig. 8. The relation between the column temperature and the peak area of $Ni(TFA)_2$ chelate. Gaschromatographic conditions are the same as in Fig. 6.

Effect of flow rate:

The optimum flow rate of the carrier gas was decided from the relation between HETP and flow rate at a column temperature of 230°C. As shown in Fig. 9, it was found that HETP was minimized near a flow rate of 41 ml/min.

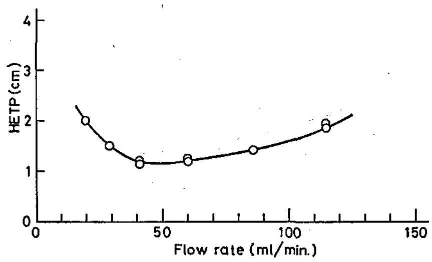

Fig. 9. The relation between HETP and the flow rate. Gaschromatographic conditions are the same as in Fig. 6.

Amount of sample and peak area:

The relations between amounts of $Ni(TFA)_2$ chelate and peak areas on the sample solutions in the presence of 7mg of iron or in the absence of iron were investigated under the following gaschromatographic conditions.

Column; Pyrex glass column (1.0m×2.5mm i. d.)

Packings; 1.95% OV-17+0.05% PEG20M on Chromosorb W AW DMCS (60/80 mesh)

Inj. and TCD temperature; 250°C

Column temperature; 230°C

H-TFA vapor generator temperature; 23.0°C (H-TFA vapor *ca.* 90 μg/ml-He)

Flow rate; 41 ml/min

TCD bridge current; 100 mA

Recorder sensitivity; 2 mV/25 cm

Chart speed; 1 cm/min

The results are shown in Fig. 10. As is clear from the figure, the peak area of Ni

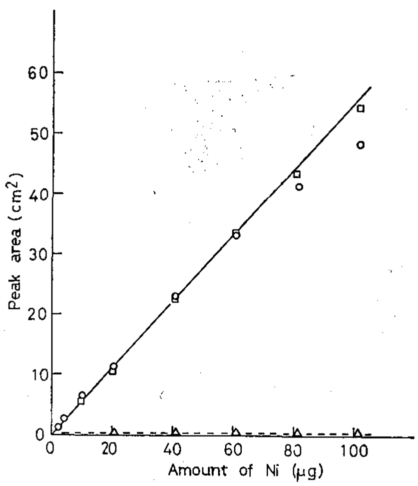

Fig. 10. The relation between amounts of $Ni(TFA)_2$ and peak areas. Gaschromatographic conditions are the same in Fig. 6. (○) in the absence and (□) in the presence of 7mg of iron in 1 ml of sample solution, (△) pure helium as the carrier gas.

$(TFA)_2$ is proportional to the concentration of $Ni(TFA)_2$, and the straight line is passed through the origin of the coordinates by using the LVGC method. From this fact, it is considered that $Ni(TFA)_2$ chelate is quantitatively eluted. Moreover, these curves in the presence and absence of iron are fitted well in the range of 2−60 μg of nickel. On the other hand, no peaks were found when the pure helium was used as the carrier gas.

Gaschromatographic Analysis of Nickel in Actual Samples

Recommended procedure:

From the results of fundamental investigation, the following analytical procedure is recommended for the gaschromatographic analysis of nickel in steel.

About 10 mg of sample is weighed exactly on a chemical balance and put into a 5 ml centrifuge tube. Subsequently, the sample is dissolved with aqua regia. After drying, the residue is dissolved with 1 ml of distilled water and 0. 2 ml of H-TFA. The pH of the solution is adjusted to 7. 5−8. 0 with diluted ammonia water. Then, nickel chelate is extracted with 0. 5 ml of *n*-butyl acetate. After extraction, *n*-butyl acetate is added to make the exact volume of the organic phase of 1 ml. Aliquots (20μl) of the organic phase are subjected to the gas chromatograph with a microsyringe.

As shown in Fig. 11, it was found that $Ni(TFA)_2$ chelate was quantitatively extracted in the pH range 7. 0−8. 5.

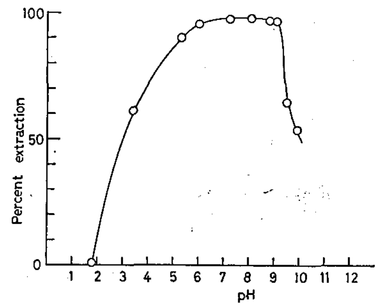

Fig. 11. The effect of the pH on the extraction of $Ni(TFA)_2$ chelate.

Interferences:

The influences of other metals in the determination of nickel were investigated, and

Table I. Interferences in the Determination of Nickel (1. 018mg Ni/ml; in the Presence of Equimolar Amount of Other Metal)

Metal	Recovery of Nickel(%)	Metal	Recovery of Nickel(%)
Tl(I)	96. 3	Hg(II)	96. 6
Si(IV)	99. 0	Ti(IV)	100. 4
Ge(IV)	98. 2	Nb(V)	99. 2
Sn(IV)	97. 3	Ta(V)	99. 7
Pb(II)	34. 8	Mo(VI)	87. 2
Bi(III)	98. 9	W(VI)	93. 2
Te(IV)	92. 5	Re(VII)	97. 3
Ag(I)	98. 9	Ir(III)	97. 0
Au(III)	96. 1	Pd(II)	96. 5
Cd(II)	38. 1	Pt(IV)	100. 0

the results are shown in Table I. The shape of the elution peak of $Ni(TFA)_2$ was remarkably influenced in the presence of Pb(II) and Cd(II), but slightly in the presence of Te(IV), Mo(VI) and W(VI), and was not interfered by the other metals.

Precision and accuracy:

The precision and accuracy of the analysis of nickel in actual samples were investigated using standard stainless steel GK-4 containing Ni 10.18%, Fe 70.72%, Cr 16.84%, Mn 1.65% and other traces. Analyses were carried out according to the analytical method mentioned above. The results are shown in Table II. As seen in the table, it was found that nickel in actual samples was determined within the error of 0.9% by gas chromatography.

Table II. Analysis of Nickel in Stainless Steel GK-4 (Ni 10.18%)

Sample taken (mg)	Nickel found (mg)	Nickel (%)	Average value and standard deviation (%)	Relative error (%)
10.00	1.006 1.007	10.06 10.07	10.09±0.10	−0.9
10.10	1.030 1.021	10.20 10.11		
10.19	1.012 1.037	9.93 10.18		

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